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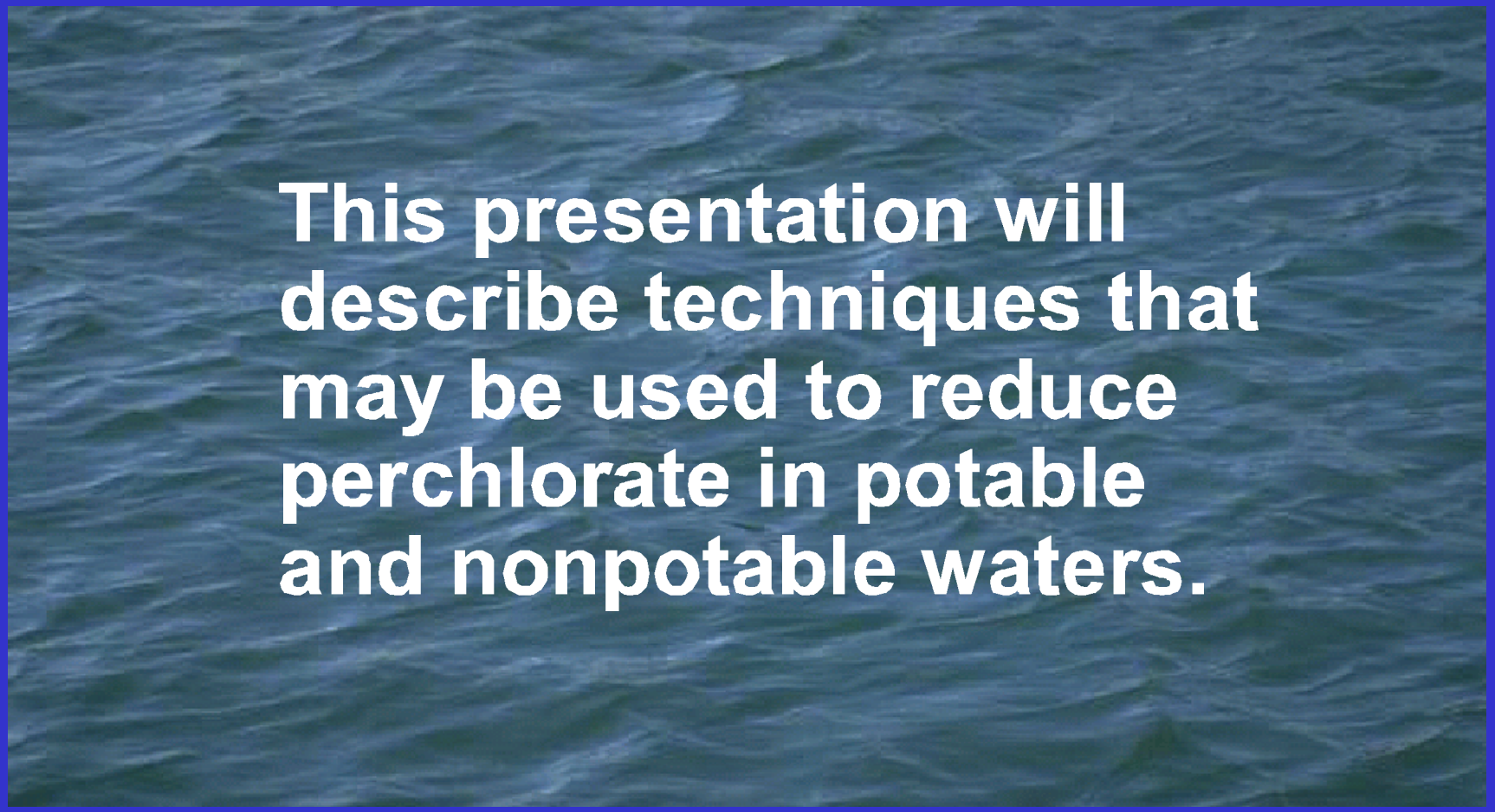
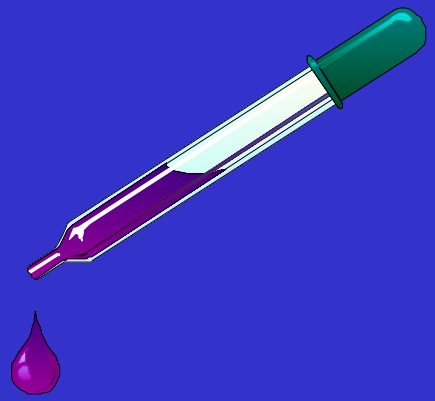
What techniques will work?



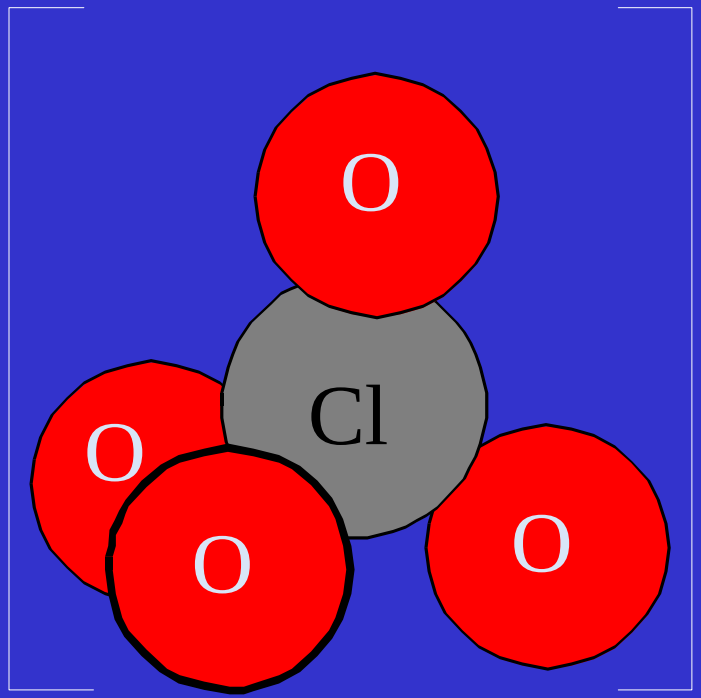
Approach

There is no one technique that will work for every case.



There is no standard or benchmark for evaluating performance.

About Perchlorate

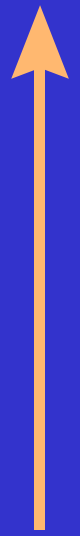


1–

- An oxyanion of chlorine
- A strong oxidizing agent (thermodynamics)
- A very sluggish species (kinetics)

Chlorine Species

Name	Oxidation State	Formula
Perchlorate	+7	ClO_4^-
Chlorate	+5	ClO_3^-
Chlorite	+3	ClO_2^-
Hypochlorite	+1	ClO^-
Dichlorine	0	Cl_2
Chloride	–1	Cl^-



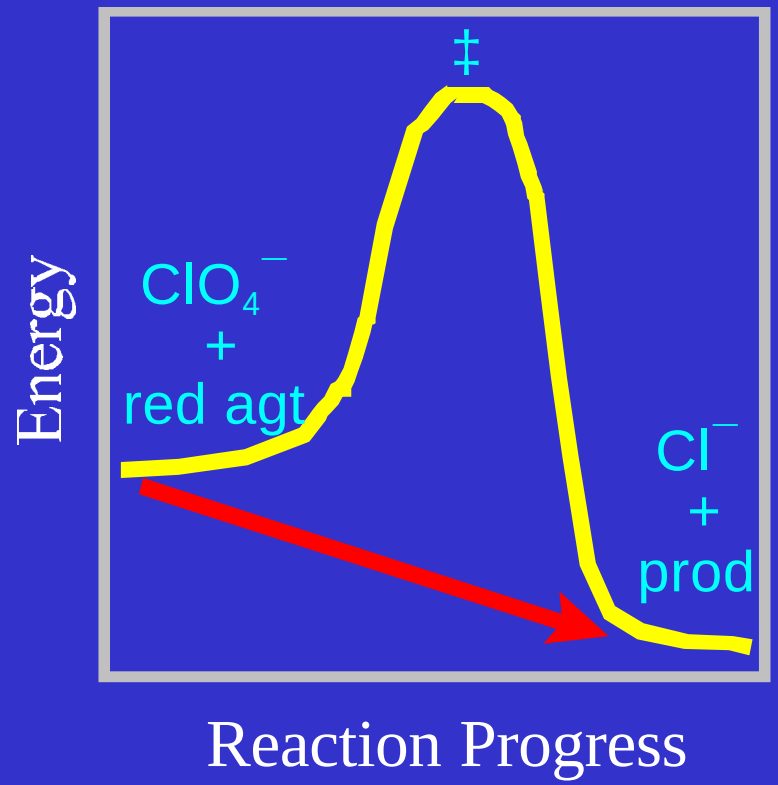
Increasing oxidizing strength

Chemical Reduction

$E° = 1.287$ volts

A reducing agent transfers electrons to the chlorine atom in a perchlorate ion, converting it to chloride.

Perchlorate Lability



In general, perchlorate reduction is very slow even though perchlorate is a strong oxidizing agent.

Common reductants (e.g., thiosulfate, sulfite) show no measurable reaction.

Labile Reducing Agents

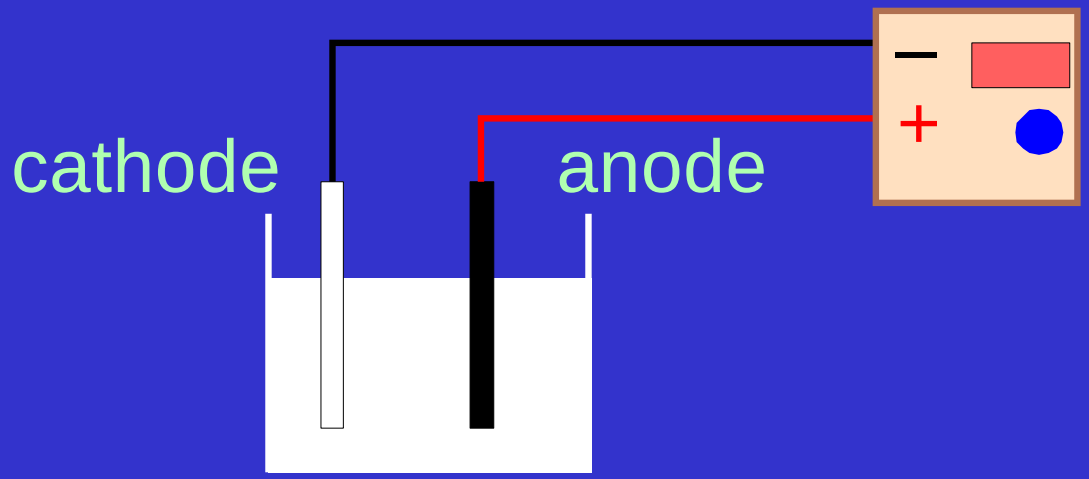
A number of air-sensitive metal species can reduce perchlorate, but they cannot be used directly in water treatment because they are still too slow and their products would have to be removed.

Titanium(III)
Vanadium(II, III)
Chromium(II)
Ruthenium(II)
Methylrhenium dioxide, CH_3ReO_2
Dimolybdenum(III), Mo_2^{6+}
Molybdenum(III)

Chemical Reduction: Problems

- Expense of materials
- Slowness of reaction
- Toxicity of by-products
- Removal of by-products

Electrochemical Reduction



Reduction

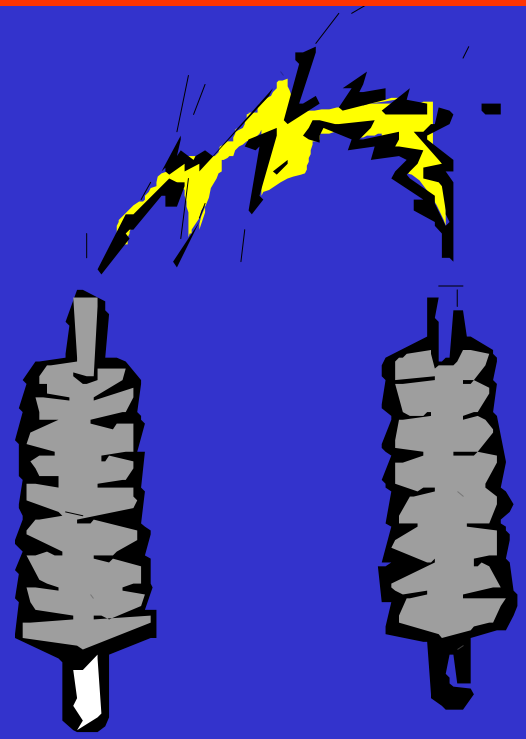
$ClO_4^- + 8\ H^+ + 8\ e^- \rightarrow Cl^- + 4\ H_2O$

Oxidation

$R^- \rightarrow R + e^-$

Electrochemistry: Anodes

- Tungsten carbide
- Ruthenium
- Platinum
- Aluminum
- Titanium
- Aluminum oxide
- Carbon (doped with Al_2O_3 or Cr_2O_3)



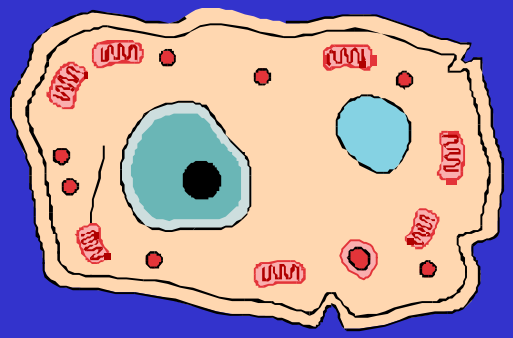
Electrochemical Reduction

- **Advantages**
  - Nontoxic by-products
  - Well-known technique
- **Disadvantages**
  - Construction/implementation expense
  - Operation expense (electricity)
  - Electrolysis of water
  - Slowness (reaction and diffusion)
  - Safety (high voltage)

Biological Reduction

The use of biological organisms, especially bacteria, to chemically reduce perchlorate to other chemical species

Perchlorate-reducing bacteria



Ideonella dechloratans
Proteobacteria
Vibrio dechloraticans Cuzensove B-1168
Wolinella succinogenes HAP-1

Biological Reduction

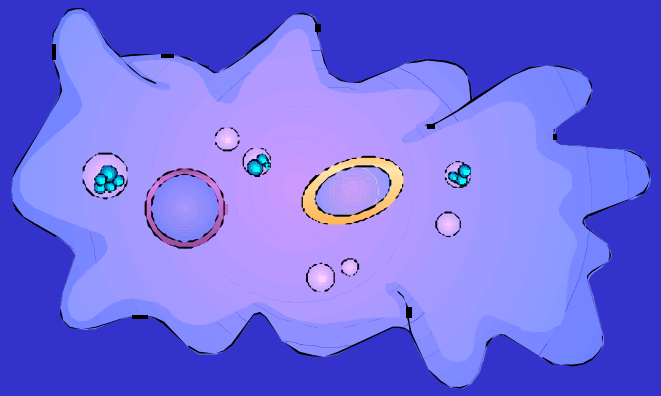
USAF, Tyndall AFB, Florida

The bacterium *Wolinella succinogenes* is capable of using perchlorate as an oxidizing agent (electron acceptor) for metabolism.

The USAF and AF Research Labs have developed a bioreactor for this purpose.

Biological Reduction

- **Advantages**
  - Nontoxic by-products
  - Versatility
  - Speed
- **Disadvantages**
  - Acceptance
  - Regulatory barriers
  - Construction/implementation costs
  - Hardiness of bacteria

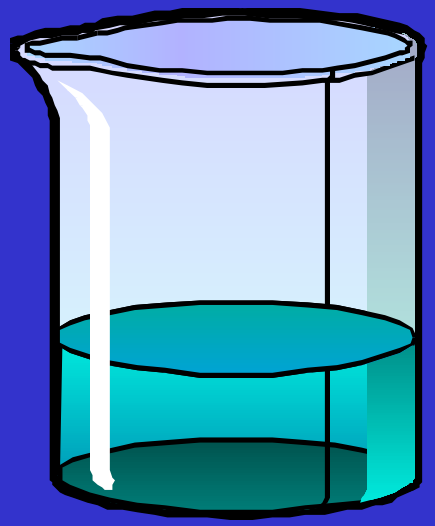


Biochemical Reduction

- Bacteria use a biological catalyst or enzyme, called a reductase, to reduce perchlorate.
- It may be possible to purify this enzyme and use it directly as a reactant for chemical reduction (addition or tethering).
- Perchlorate reductases evolved from nitrate reductases used by nitrogen-fixing bacteria (e.g., those in legumes).

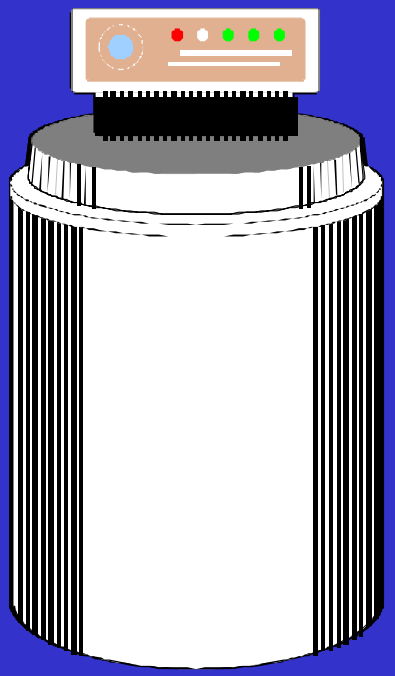
Biochemical Reduction

- **Advantages**
  - No toxic perchlorate by-products
  - Fast reaction time
  - High effectiveness
- **Disadvantages**
  - High expense in producing enzyme
  - High maintenance
  - Difficult implementation
  - Enzyme by-products unstudied



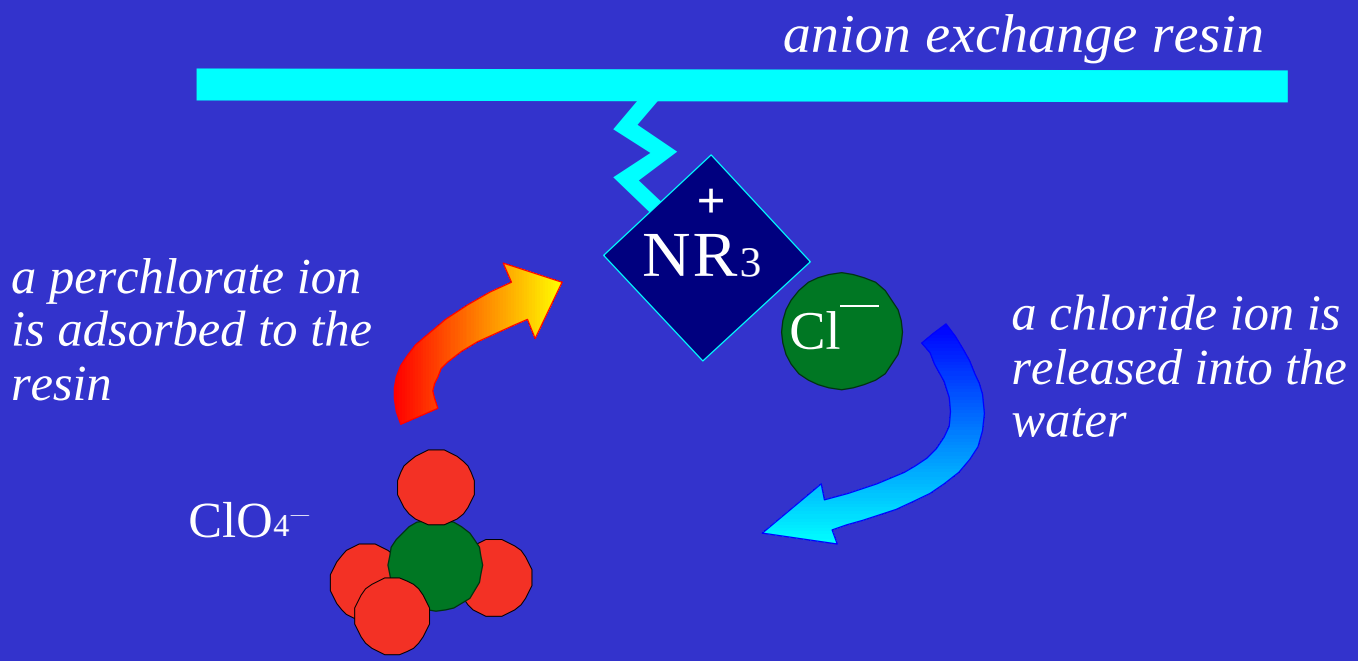
Physical Separation

- **Anion exchange**
- **Membrane processes**
  - Nanofiltration
  - Reverse osmosis
  - Electrodialysis



Anion Exchange

A positively charged resin is used to exchange the perchlorate ion for a harmless chloride ion.



Ion Exchange for Pertechnetate

Oak Ridge National Laboratory
Oak Ridge, Tennessee

Selective pertechnetate (TcO_4^-) removal to parts per trillion (pg mL^{-1}) levels

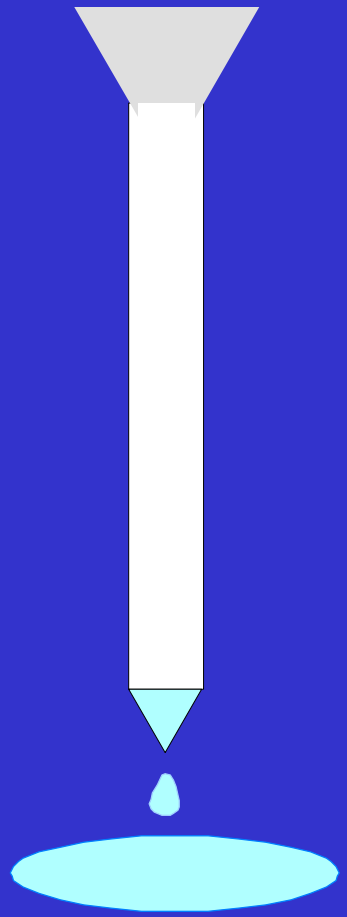
Ion Exchange for Nitrate

Anion exchange is used to remove nitrate from water.

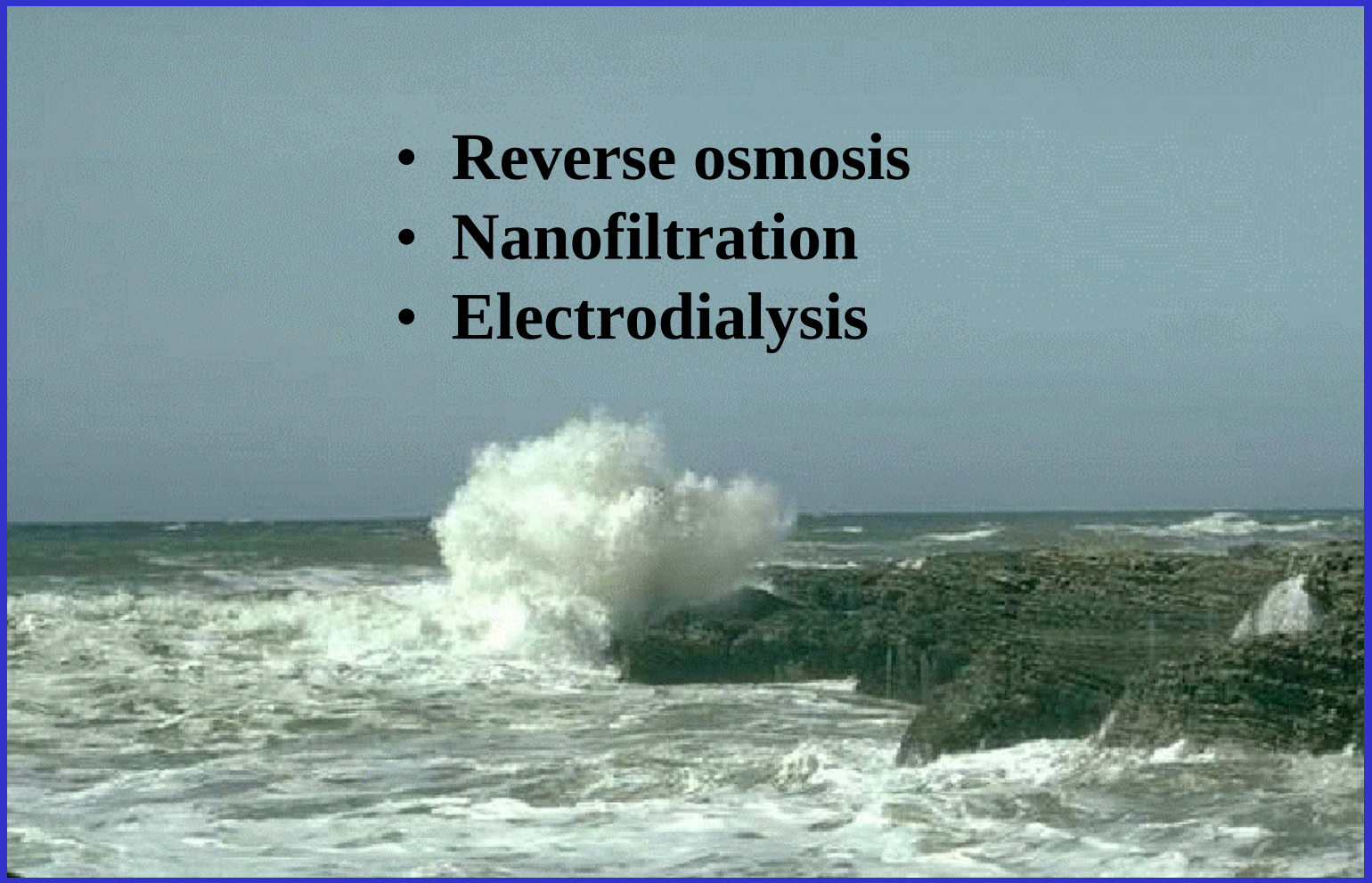
- Nitrate-selective resins already exist. NO_3^-
- Perchlorate and nitrate have similar physical properties (charge, size, aquation).
- Therefore, these resins are expected to be effective in removing perchlorate.
- However, permissible nitrate concentrations are much higher than the perchlorate action level.

Anion Exchange

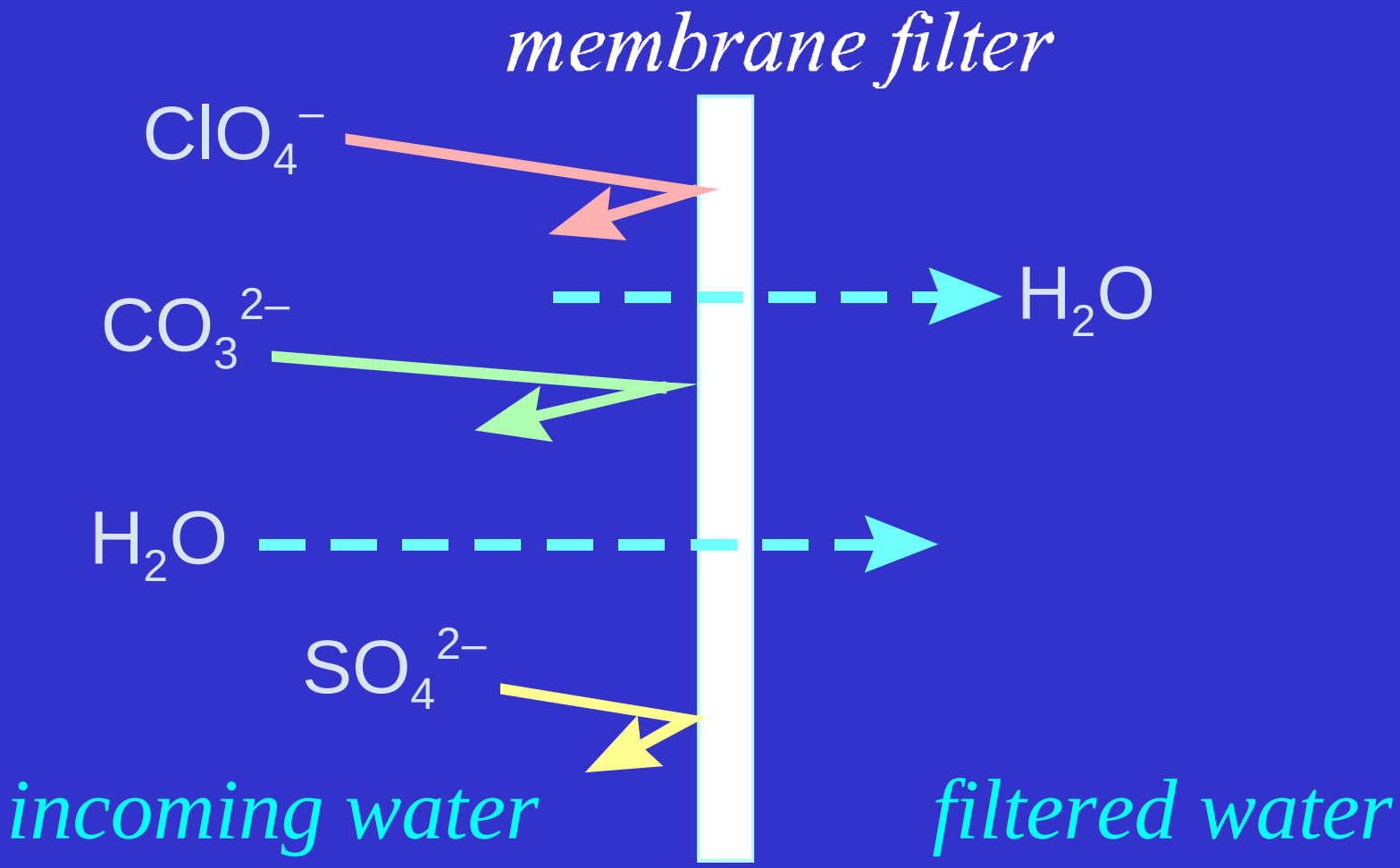
- **Advantages**
  - Reasonable operating costs
  - Well-developed technique
  - Easy implementation
  - Effectiveness
- **Disadvantages**
  - Waste disposal from regeneration
  - Moderate selectivity
  - Distribution system effects
  - Resin lifetime



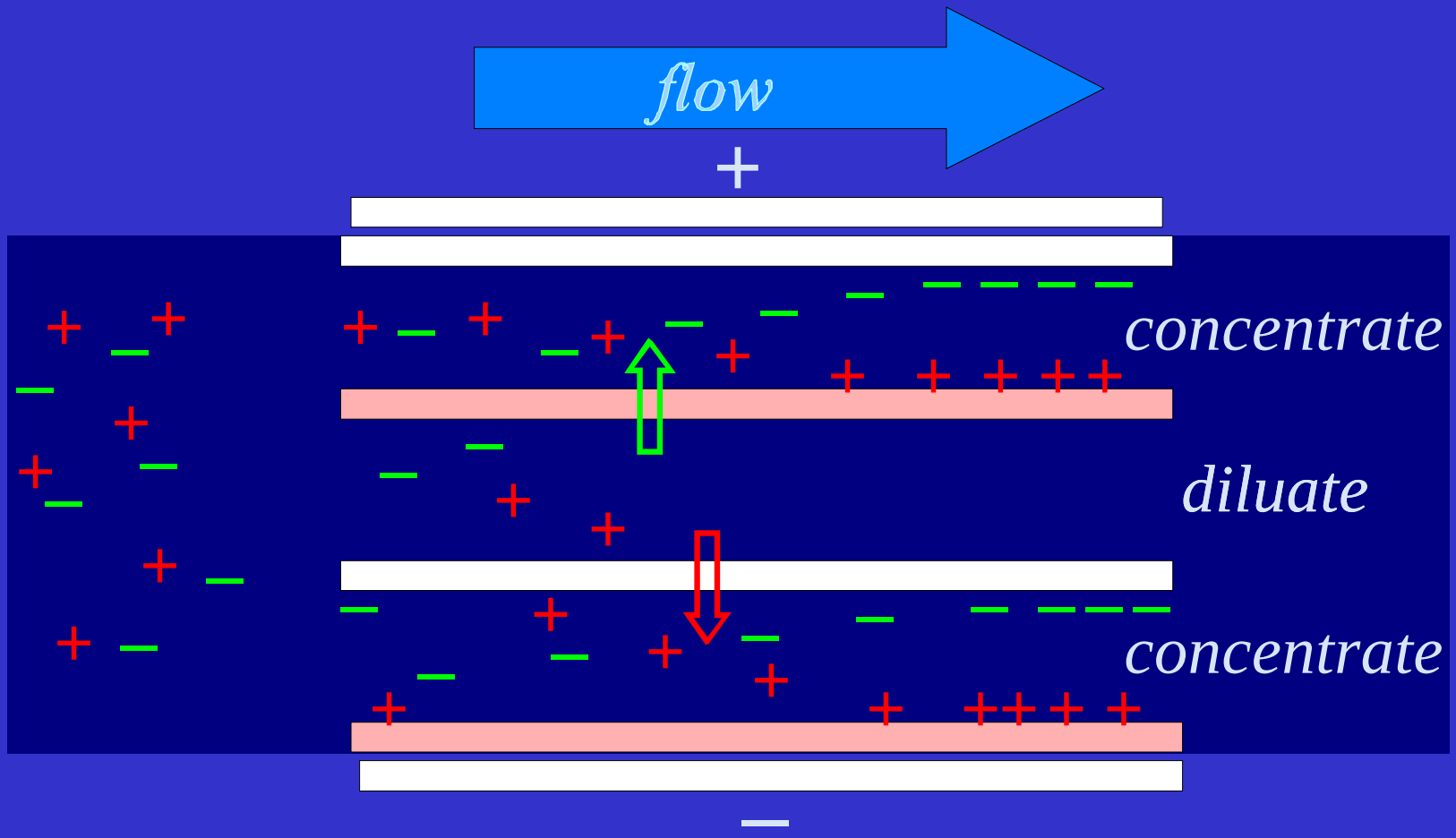
Membrane Techniques



Reverse Osmosis/Nanofiltration

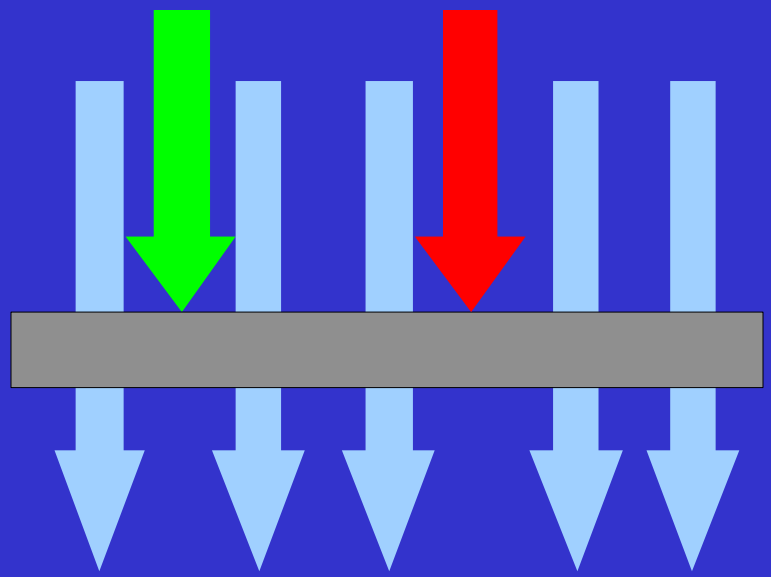


Electrodialysis



Membrane Techniques

- **Advantages**
  - High effectiveness
  - Low operating cost
  - High throughput
  - Easy implementation
- **Disadvantages**
  - Low selectivity
  - Distribution system effects
  - Palatability
  - Waste effluent disposal

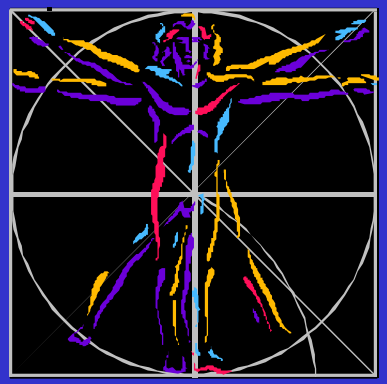


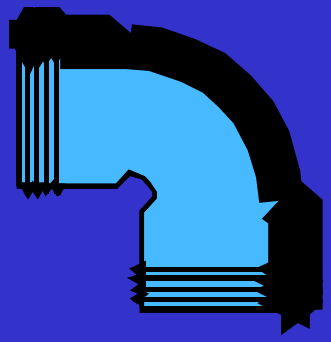
Under Investigation

- Reverse Osmosis and Nanofiltration
- Ozone/GAC (Chemical Reduction?)
- Biological Reduction
- Anion Exchange

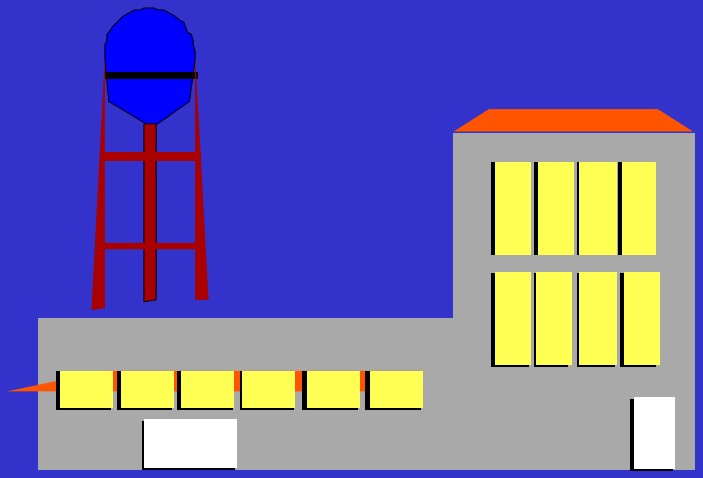
General Considerations

- **Incomplete health effects studies**
- **Success at reaching trace concentrations**
- **Distribution system effects**





General Considerations

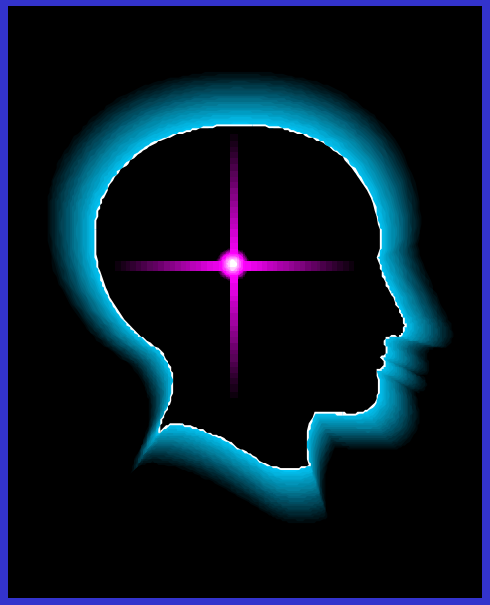


- **Effects on other treatment processes**
- **Effects from other treatment processes**
- **Reliability**

General Considerations

- Palatability
- Time
- Expense

Customization



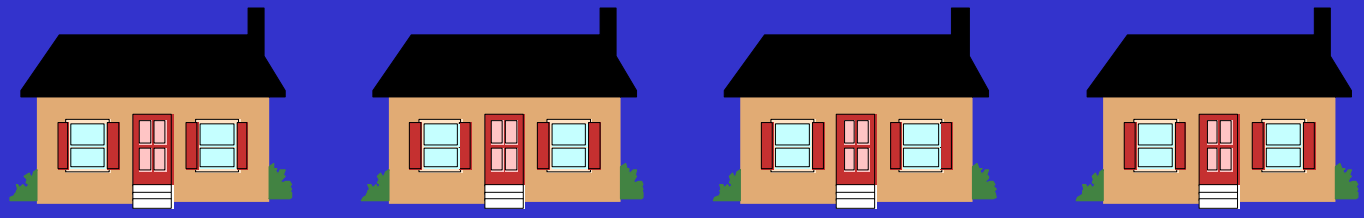
The best solution for a specific situation is likely to be a combination of technologies.

- Anion exchange + bioremediation
- Nanofiltration + blending

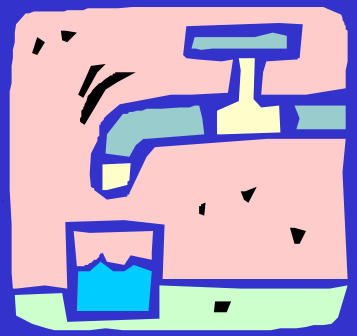
Small Systems

Small systems may benefit from a number of techniques that will not work in large systems.

- Reverse osmosis
- Anion exchange

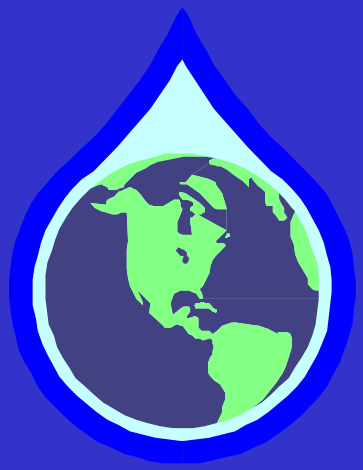


Point of Use



- Some techniques lend themselves to point-of-use devices.
- Both anion exchange and RO may be used at individual sites or for very small systems.
- No standards presently exist for purification systems; however, that could be rectified fairly

Directions



Congress has appropriated $2 million to the East Valley Water District for studies on perchlorate.

The American Water Works Association Research Foundation has requested proposals.

EPA anticipates an initiative in fiscal year 2000.

Closing

- **Perchlorate is unlike other contaminants already regulated.**
- **Effective management will require long and short term responses.**
- **The best solutions will**
- **only come about through**
- **continued cooperation**
- **among state, local, and**
- **federal agencies.**